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(19) (CA) **CANADIAN PATENT** (12)

(54) FOOD FILM WRAP

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ABSTRACT OF THE DISCLOSURE

A packaging film wrap useful in preserving food substances containing oils, fats and chromoproteins is disclosed having a synergistic preserving mixture on the film surface wherein the mixture is contained in a carrier substance and consists of at least one antioxidant and an antimicrobial agent. The antioxidant is preferably ascorbic acid or isoascorbic acid and the antimicrobial agent is preferably a mixture of methyl and propyl esters of parahydroxybenzoic acid, wherein the weight ratio of the antimicrobial agent to the antioxidant is within the range of 1:1 to 5:1.

The embodiments of the invention in which an exclusive property or privilege is claimed are as follows:

1. A packaging film useful in preserving food substances containing oils, fats, and chromoproteins, comprising a flexible substrate material having thereon a surface coating consisting essentially of 0.18-0.22 pounds per 1000 square feet of film surface area of a synergistic preserving mixture contained in a polyvinyl alcohol dispersion, said mixture consisting of:
  - (a) at least one antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid; and
  - (b) an antimicrobial agent consisting of a blend of equal parts by weight of the methyl and propyl esters of parahydroxybenzoic acid, the weight ratio of said antimicrobial agent to said antioxidant falling within the range of about 1:1 to 5:1.
2. The film of Claim 1 wherein said coating contains per 1000 square feet of surface area 0.18 pounds of a mixture containing equal parts by weight of the methyl and propyl esters of parahydroxybenzoic acid and 0.04 pounds of ascorbic acid.
3. The film of Claim 1 wherein said substrate material is polypropylene or polyethylene.



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ABSTRACT OF THE DISCLOSURE

A packaging film wrap useful in preserving food substances containing oils, fats and chromoproteins is disclosed having a synergistic preserving mixture on the film surface wherein the mixture is contained in a carrier substance and consists of at least one antioxidant and an antimicrobial agent. The antioxidant is preferably ascorbic acid or isoascorbic acid and the antimicrobial agent is preferably a mixture of methyl and propyl esters of parahydroxybenzoic acid, wherein  
10 the weight ratio of the antimicrobial agent to the antioxidant is within the range of 1:1 to 5:1.

BACKGROUND OF THE INVENTION

During recent years there has been a great deal of development in the art of packaging such food items as meats, poultries, vegetables and dairy products for the purpose of attractively displaying and additionally preserving such food items while on display at various food stores.

It has been known to use such antioxidant agents as ascorbic acid or isoascorbic acid in the specific preservation of the color of food products. For example, U.S. Patent  
20 No. 2,906,646 to Smith et al discloses the use of ascorbic acid as an antioxidant useful in preserving such food substances. It is also disclosed that benzoic acid esters can be used in combination with such antioxidant substances on food wrapping materials. U.S. Patent No. 2,979,410 to Parlour discloses the use of isoascorbic acid as a fungicidal agent as well as an antioxidant on food film wrappings for preserving meats. Additionally, U.S. Patent No. 2,858,225 to Gooding et al  
30 discloses a package treating process in which the wrapper material is impregnated with a fungistat of low-volatility



to render the package wrapper useful in preventing spoilage of various food products due to the growth of molds on the surface of such products. A specific fungicidal agent mentioned is parahydroxybenzoic acid. Also, U.S. Patent No. 3,134,687 to Lück discloses a preservative packaging material having calcium sorbate incorporated into a polyvinyl alcohol carrier substance. Disclosure of various antioxidants useful in food preservation are provided in U.S. Patent Nos. 2,709,657 to Campbell, 2,843,497 to Stuckey et al and 3,052,553 to McKillip et al.

10                   It is to be noted that two separate mechanisms for spoilage of food substances containing oils, fats and chromo- proteins can occur either simultaneously or separately. In one case, spoilage can occur due to the growth of microbiological contaminants such as bacteria, fungi, molds, mildew, etc. In the other case, spoilage can additionally occur due to oxidation which causes certain chemical changes in the oily substances of the food product rendering them rancid or less desirable due to color change (e.g. the loss of red color in meats or meat products).

20                   SUMMARY OF THE INVENTION

                  In an attempt to overcome such problems with respect to packaging food products, Applicant has surprisingly discovered that combinations of specific antioxidants and antimicrobial agents contained on a flexible packaging material are more effective as a food preserving composition than either of the ingredients taken separately. Specifically, a packaging film useful in preserving food substances containing oils, fats and chromoproteins is herein disclosed comprising a flexible substrate material having thereon a surface coating  
30                   consisting essentially of 0.18-0.22 pounds per 1000 square feet of film surface area of a synergistic preserving mixture

contained in a polyvinyl alcohol dispersion, said mixture consisting of:

- (a) at least one antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid; and
- (b) an antimicrobial agent consisting of a blend of equal parts by weight of the methyl and propyl esters of parahydroxybenzoic acid, the weight ratio of said antimicrobial agent to said antioxidant falling within the range of about 1:1 to 5:1.

10

Preferably, the coating contains per 1000 square feet of surface area, 0.18 pounds of a mixture containing equal parts by weight of the methyl and propyl esters of parahydroxybenzoic acid and 0.04 pounds of ascorbic acid. Also, the substrate material is either polyethylene or polypropylene.

#### DETAILED DESCRIPTION OF THE INVENTION

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Insofar as the particular types of antioxidant substances which have been found to be most useful, ascorbic acid and isoascorbic acid are preferred. Additionally, it has been found that the methyl and propyl esters of parahydroxybenzoic acid are preferred as antimicrobial agents. Based upon experimental work conducted in using coatings of these materials in various combinations on flexible food packaging films, it has additionally been found that surprisingly effective preserving mixtures are obtained wherein a concentration of 0.18 to 0.22 pounds per 1000 square feet of film surface area are used and the weight ratio of antimicrobial to antioxidant falls within the range of about 1:1 to 5:1.

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Since these parahydroxybenzoic acid esters are relatively water insoluble, it has been found necessary to disperse them in combination with the relatively water-soluble ascorbic or isoascorbic acid in a carrier material which is water soluble and can act as a vehicle for transfer of the preserving mixture from the film wrap surface and onto the food product surface which has a residual moisture content and is in contact therewith.

10 Although polyvinyl alcohol is the preferred carrier material for the active preserving ingredients, other water-sensitive materials could be used, so long as they are capable of solubilizing the antimicrobials and additionally either soluble in water or exhibit some degree of sensitivity on contact with water (e.g. is capable of becoming moistened or swellable). Examples of other such water-sensitive materials are carboxymethylcellulose, polyvinylmethyl ether, algin, alginates, cellulose gum, gelatin, gum arabic, gum acacia and the like. Although there is no critical concentration for the carrier, it is inherently necessary that enough be present to effectively  
20 form on the film surface a coating dispersion containing the active preserving ingredients (i.e. the anti-oxidant and the antimicrobial agents).

Also, although polyethylene and polypropylene are preferred as the food wrapping materials or substrates, other useful flexible substrate materials can include regenerated cellulose, saran, rubber hydrochloride films, vinyl films, polystyrene, cellulose acetate, "Mylar"\* (polyethylene terephthalate produced by DuPont), trifluoroethylene films, cellophane and various blends of polyvinyl chloride.

\* Trade Mark

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Generally, the carrier and active preserving agents are initially dissolved in a solvent mixture to form a coating material for application to the flexible substrate in preparing the packaging film. The coating can be applied by any of the conventional methods such as by dipping the substrate in the coating composition in which case both sides of the film are coated. Another method for applying the coating to the film is by spraying it on to a moving web of film. In this method, either one or both sides of the film are coated.

10 After application of the coating to the film, the solvents are evaporated by drying the coated film. Such drying may be effected by conventional means including heating or infra-red radiation. After such drying, the film contains the carrier having dispersed therein the anti-oxidant and the anti-microbial agents. There is no criticality to the choice or proportion of solvents so long as they aid in solubilizing the carrier to promote the formation of the dry dispersion of the actives in the carrier when applied as a coating on a film. Typical solvents might include ethanol, and larger chain

20 ethers, p-glycol ethers, acetone, ethyl ether, propylene glycol, glycerol, water and mixtures thereof.

The following examples are provided to illustrate the present invention and should not be deemed as limiting the scope of which is defined by the appended claims. Generally, the coating composition can be applied at a rate which can vary from about 0.1-4 pounds per 1000 square feet of film surface. Preferably, about 1 pound per 1000 square feet of film surface is used.



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A typical coating formulation is exemplified by the following:

		<u>Weight %</u>
	Deionized water (solvent)	49.00
	Polyvinyl alcohol (carrier)	20.00
	Methyl ester of parahydroxybenzoic acid (antimicrobial)	7.50
	Propyl ester of parahydroxybenzoic acid (antimicrobial)	7.50
10	Ascorbic acid (antioxidant)	3.00
	Ethanol (solvent)	7.75
	Propylene glycol (solvent)	5.25
		<hr/> 100.00

## EXAMPLE 1

Seven coated polypropylene films (Groups 1-7 below) were prepared using coating compositions having the following weight percent of active ingredients in the coating composition just prior to application to the films:

20	<u>Group</u>	<u>Weight % of 50/50 blend of methyl and propyl esters of parahydroxybenzoic acid</u>	<u>Weight % Ascorbic Acid</u>
	1	18	4
	2	22	0
	3	0	18
	4	0	22
	5	15	3
	6	18	0
	7	15	0
	8	0	0

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The eighth group represents uncoated polypropylene film. The coating compositions were applied at the rate of 1 pound of composition per 1000 square feet of film surface area, and after appropriate drying to remove solvents, there remained  
5 coatings on the eight film surfaces containing the initial concentrations of active ingredients contained in a polyvinyl alcohol dispersion.

Ten slices of boneless beef roast were individually wrapped using Group 1 coated film, refrigerated at 40°F, and  
10 observed during a 14-day period while at room temperature (25°C). None of the slices were opened until the final day of the test. The spoiled areas were determined by visual inspection for color change, change due to putrefication, darkening of the meat and slime formation. The individual slices were  
15 examined daily and at the first sign of any spoilage (denoted as any visual defect that would render the meat unfit for sale) on a particular piece, it was classified as spoiled. The meat slices had a relatively high initial bacteria count of 208,000 bacteria per square inch of meat surface. The same observa-  
20 tions were made for coated film Groups 2-7 and uncoated film (Group 8), each group being used to wrap 10 slices of boneless beef roast having the same initial bacteria count. The results are given in Table 1 below.

TABLE 1

Group	Days of Stability <sup>1</sup> at 25°C	Synergism <sup>2</sup> (in days)	Total Spoilage <sup>3</sup> (days) at 25°C	% of Area Spoiled <sup>4</sup> After	
				10 days	14 days
1	5	3	9	36	83
2	3	-	10	67	80
3	1	-	7	100% spoilage after 9 days	-

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Group	Days of Stability at 25°C <sup>1</sup>	Synergism <sup>2</sup> (in days)	Total Spoilage <sup>3</sup> (days) at 25°C	% of Area Spoiled <sup>4</sup> After		
				10 days	14 days	
5	4	1	-	7	100% spoilage after 9 days	
	5	4	2.5	9	54	88
10	6	2	-	8 slices spoiled after 10 days	25	43
	7	1	-	7 slices spoiled after 8 days	33	49
15	8 (control)	1	-	4	100% spoilage after 7 days	-

- 20 Notes: 1- "Days of Stability" means number of days after test begun when any meat slice showed any sign of spoilage within a group.
- 2- "Synergism" (S) is defined as  $S = A - 1/2(B+C)$  wherein A is the stability of the wrapped meat where the film wrap coating contains the combination of the 50/50 blend of methyl and propyl esters of parahydroxybenzoic acid and ascorbic acid; B is the stability of the wrapped meat where the film wrap coating contains only the 50/50 blend of esters in quantities equal to that of "A"; and C represents the stability of the wrapped meat where the film wrap coating contains only the ascorbic acid in quantities equal to "A".
- 25 3- "Total Spoilage" means number of days after test begun when all slices in a group showed any signs of spoilage.
- 30

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4- "% of Area Spoiled" means percentage of total area of all meat slices in a group observed to be spoiled after indicated days.

## EXAMPLE 2

5 The procedure of Example 1 was repeated except that six slices of meat were used per group and there were only 4 groups having the following weight percent of active ingredients in the coating composition just prior to application to the films:

10	Group	Weight % of 50/50 blend of methyl and propyl esters of <u>parahydroxybenzoic acid</u>	Weight % <u>Ascorbic Acid</u>
	1	18	0
	2	18	2
15	3	18	4
	4	20	0
	5 (Control)	0	0

The fifth group represents uncoated polypropylene film. Also, the initial bacteria count on the meat slices was approximately half that for Example 1. The results are given in Table 2 below with the terms having the same meaning as previously defined.

TABLE 2

25	Group	Days of Stability at 25°C	Total Spoilage (days) at 25°C	% of Area Spoiled After	
				10 days	14 days
	1	5	13	48	75
	2	6	9	36	73
	3	8	14	5	48
30	4	4	10	72	98
	5 (Control)	1	4	92	100% spoilage after 11 days

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It should be noted that the predominant mechanism for spoilage depicted in the results for Table 1 was probably due to bacterial action rather than oxidation in view of the relatively high initial bacteria count on the meat slices. Whereas, the results in Table 2 reflected both oxidative spoilage of many of the beef slices (fading from red to a gray pork color) as well as bacterial spoilage, in view of the lower initial bacteria count which was about one half that for Example 1. The films in Table 1 coated with both antimicrobial and antioxidant agents (e.g. Groups 1 and 5) did not appear to be quite as effective as those films containing only an antimicrobial (e.g. Groups 6 and 7), insofar as average percent of total area of meat slices spoiled over an extended period of time. However, the films in Table 2 coated with an antimicrobial and antioxidant (e.g. Groups 2 and 3) were somewhat more effective regarding this aspect than those films containing only the antimicrobials (e.g. Groups 1 and 4) where spoilage was attributable to two mechanisms (i.e. bacterial action and oxidation).

### EXAMPLE 3

Nine coated polypropylene films (Groups 1-9 below) were prepared using coating compositions having the following weight percent of active ingredients in the coating composition just prior to application to the films:

Group	Weight % of 50/50 blend of methyl and propyl esters of parahydroxybenzoic acid	Weight % Ascorbic Acid
1	0	18
2	3	15
3	9	9
4	12	6
5	14	4

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Group	Weight % of 50/50 blend of methyl and propyl esters of parahydroxybenzoic acid	Weight % Ascorbic Acid
6	15	3
5	7	18
8	0	3
9	15	0
10 (Control)	0	0

The tenth group represents uncoated polypropylene film. The coating compositions were applied at the rate of 1 pound of composition per 1000 square feet of film surface area, and after appropriate drying to remove solvents, there remained coatings on the nine film surfaces containing the initial concentrations of active ingredients contained in a polyvinyl alcohol dispersion.

Six slices of meat were wrapped with the film for each of the ten groups and maintained at 40°F during the test period. On the seventh day and again on the twelfth day, 2 slices were randomly removed from each group for bacterial observations at room temperature (25°C). Thus, average spoilage ratings for each group were based on 6 slices up to and including the seventh day, 4 slices for the eighth day up to and including the eleventh day, and 2 slices for the twelfth day to fourteenth day. The following spoilage scale was used for average evaluations:

<u>Spoilage Rating</u>	
100% spoilage of total area of slices -	0
75% spoilage of total area of slices -	1
50% spoilage of total area of slices -	2
25% spoilage of total area of slices -	3
5% spoilage of total area of slices -	4

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The results are given in Table 3 below:

TABLE 3

Group		Average Spoilage Ratings After		
		7 days	11 days	14 days
5	1	4.16	2.25	1.0
	2	3.24	1.25	1.0
	3	5.00	4.00	3.0
	4	5.00	4.80	2.0
	5	4.84	4.25	2.0
10	6	5.00	4.75	4.0
	7	4.67	4.50	3.5
	8	4.50	1.50	1.0
	9	5.00	4.50	2.0
	10 (Control)	2.84	1.00	0.5

15 A definition for synergism similar to that for Table 1 is used, namely,  $S = A - 1/2 (B+C)$ , where A is the spoilage rating of the wrapped meat where the film wrap coating contains the combination of the 50/50 blend of methyl and propyl esters of parahydroxybenzoic acid and isoascorbic acid; B is the spoilage rating of the wrapped meat where the film wrap coating contains only the 50/50 blend of esters in quantities equal to that of "A"; and C represents the spoilage rating of the wrapped meat where the film wrap coating contains only the isoascorbic acid in quantities equal to "A".

25 With this definition in mind, the combined average spoilage ratings of the individual active ingredients, i.e.  $1/2 (B+C)$ , is given below for 7, 11 and 14 days where B represents the spoilage ratings in Table 3 for Group 1 containing only antimicrobials and C represents the spoilage ratings in Table 3 for Group 2 containing only antioxidant.

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## Rating Period      Combined Average Ratings for Groups 1 and 2

7 days	4.41
11 days	3.37
14 days	2.25

5      It is observed that the ratings given in Table 3 for Groups 3 and 6 are greater for each Rating Period compared to the combined ratings given above indicating synergism. The ratings for Groups 4 and 5 are greater than the combined ratings for 7 and 11 days, but slightly lower for 14 days, again indicating synergism.

10

### EXAMPLE 4

Polypropylene films are coated using coating compositions having specific concentrations of active ingredients in the coating composition just prior to application to the films and resulting in the following spoilage ratings given in Table 4 below:

15

TABLE 4

	<u>% Isoascorbic Acid</u>	<u>% p-hydroxybenzoic acid esters (50% methyl, 50% propyl)</u>	<u>Spoilage Rating After 10 Days</u>
20	5	0	5
	3.8	0	5
	2.5	0	4
	1.25	0	3.5
	5.0	18	2.5
25	3.8	18	1
	2.5	18	1
	1.25	18	2
	2.5	18	0 (after 6th day)
	0	10	3 (after 6th day)
30	0 (Control)	0	5 (after 6th day)



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The coating compositions were applied at the rate of 1 pound of composition per 1000 square feet of film surface area, and after appropriate drying to remove solvents, there remained coatings on the 10 film surfaces containing the initial concentrations of active ingredients contained in a polyvinyl alcohol dispersion. The spoilage rating system used is that "0" means excellent (i.e. negligible spoilage) and "5" means very poor (i.e. substantial spoilage).

**SUBSTITUTE**  
***REMPLACEMENT***

**SECTION is not Present**  
***Cette Section est Absente***